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Surface structures of silicon and germanium

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1. INTRODUCTION

The detailed study of semiconductor surfaces is of considerable significance in modern technology today (Many *et al* 1965). Although the properties of the real surfaces are reasonably well understood there is still a great deal of uncertainty surrounding the exact nature of the ideal surfaces of semiconductors and how gases are absorbed onto such surfaces.

In these experiments silicon and germanium were cleaved under ultra high vacuum and then the cleaved surfaces were exposed to both oxygen and subsequent heat treatment. LEED and spot photometric measurements were taken of the surfaces These results supported one of the recently proposed surface models and gave further understanding to the absorbed state of oxygen on silicon and germanium surfaces. AES measurements of the cleaved surfaces were reported earlier (Palmborg 1968, Grant & Haas 1969, Ridgway & Haneman 1970)

2. EXPERIMENTAL TECHNIQUES

The samples were cleaved under ultra high vacuum ($\sim 10^{-10}$ Torr) and were examined using a standard Varian LEED optics. The crystals were cleaved on the (111) plane by a new technique described elsewhere (Ridgway & Haneman 1969a). The cleavages gave good diffraction patterns with usually one strongly preferred orientation. The preferred direction (structure orientation) can be correlated with the cleavage direction (direction of the tear marks) as previously reported (Ridgway & Haneman 1969b). The crystal holder used for multiple cleavages is shown in figure 1

Intensity measurements were made using a precision photoelectric telescope with the light from the centre of the telescope's field being detected by a photometer using a RCA 931A phototube.

Oxygen was exposed to the freshly cleaved surfaces via a pure silver diffusion leak For low oxygen exposures ($< 10^{-7}$ torr min) the pressure was measured on the getter ion pump. For higher pressures (10^{-7} torr min to several torr min) the getter ion pump was switched off and the pressure was measured using an ionization gauge (G.E type VH20) with a low temperature (1000°C) thoria coated irridium filament.

The crystals could be heated either by thermal conduction or by directly passing current through the sample. The latter method was most effective for higher temperatures (> 800°C). The temperature was measured using an infra red pyrometer which had a range of 60°C to 1700°C. The calibration of Jona (1966) for this particular radiation pyrometer (2·0–2·6μ) for Si, Ge and GaAs plus the emissivity estimates were used in these experiments.

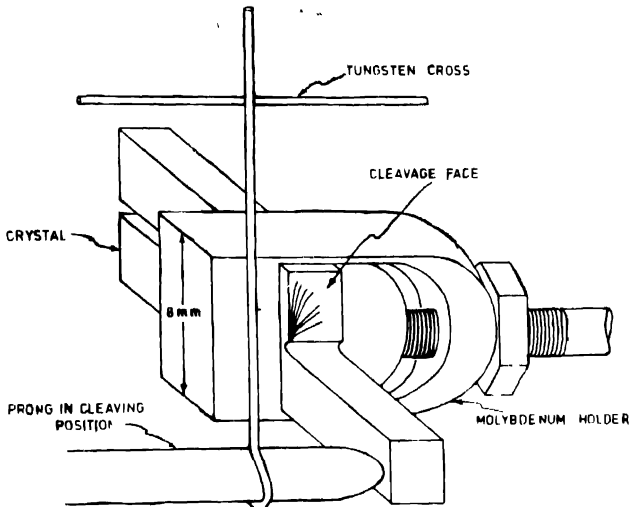

Fig. 1. Crystal in molybdenum mount illustrating multiple cleavages. The tungsten cross was used to locate the electron beam position on the cleavage surface.

3 Results

a) *Oxygen exposure*.

The cleaved surface for both Si and Ge gave the expected (2 × 1) surface structure (Lander, Gobeli & Morrison 1963). The two dimensional index scheme due to Haneman (1968) using a nonrotated 2 × 1 cell with the spot labelling is given in figure 2.

The intensity of the spots observed on this 2 × 1 LEED pattern depended critically on the cleavage. If either a very small atomically smooth area was obtained or the crystal fractured rather than cleaved, the resulting pattern was correspondingly less intense.

The results of oxygen exposure for both the cleaved surface of Si and Ge were qualitatively similar and are summarized together. The 1/2 orders on

the cleaved 2×1 pattern disappeared after exposure to 10^{-7} torr min of oxygen for Si and 5×10^{-7} torr min of oxygen for Ge. A corresponding increase in the background on the screen accompanied the increase in oxygen exposure. With increasing exposure (10^{-6} to 10^{-2} torr min) the integral orders weakened. The spot pattern could only be observed at increasingly higher voltages. At 10^{-1} torr min of oxygen, the integral orders disappeared on both surfaces, leaving no pattern.

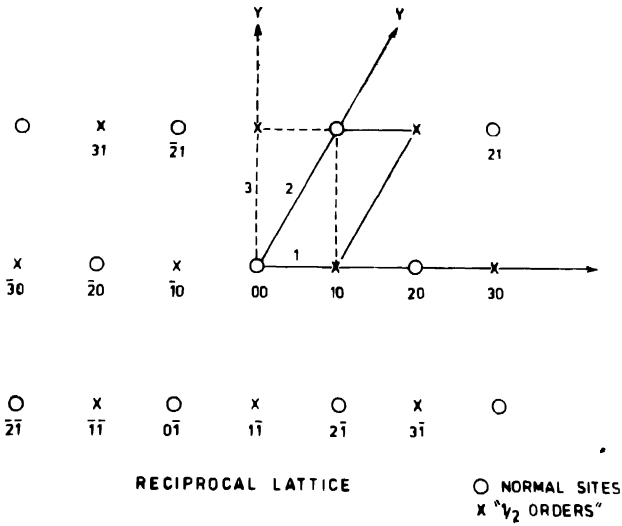

Fig. 2. The two-dimensional index scheme of Haneman (1968) for the cleaved surface LEED pattern.

b) *Heat Treatment*

Both the Si and Ge surfaces, after exposure to 10^{-1} torr min of oxygen (disappearance of LEED pattern), were subjected to heat treatment For Si the following results were found Heat treatment at $\sim$ 900°C for several seconds restored the integral orders Further heating for 35 minutes of 920°C gave an entirely new pattern having 1/3 orders The structure could be indexed as $\sqrt{3}\times\sqrt{3}$ (R30°) relative to the original 1×1 cell It remained unchanged when heated at 915°C in an atmosphere of oxygen at 1×10^{-2} torr for 5 minutes. However when the surface was exposed to 2×10^{-6} torr min of oxygen without further heating, the fractional orders weakened. An exposure of 10^{-5} torr min of oxygen did cause the fractional orders to disappear, leaving only the integral orders.

When the crystal was further heated at 900°C for 10 minutes in an atmosphere of oxygen (pressure 10^{-6} torr) the integral orders were observed to remain. These changes are indicated schematically in table 1.

Table 1 Observed Changes in the LEED pattern from cleaved surfaces of Si and Ge after various oxygen exposures and heat treatment.

Surface	LEED Pattern	Oxygen Exposure (Torr mm)	Heat treatment	
			Temperature (°C)	Time (minutes)
Si	2×1			
	1×1	10^{-7}		
	—	10^{-1}		
	1×1		900	Seconds
	$\sqrt{3}\times\sqrt{3}$		920	35
	$\sqrt{3}\times\sqrt{3}$	10^{-2}	915	5
	$\sqrt{3}\times\sqrt{3}$	2×10^{-6}		
	(weakened fractional orders)			
	1×1	10^{-5}		
	1×1	10^{-6}	900	10
Ge	2×1			
	1×1	5×10^{-7}		
	-	10^{-1}		
	—		360	5
	—		450	5
	1×1		550	3
	1×1		800	Seconds
	1×1	10^{-5}	200	10
	1×1	10^{-4}	300	10
	1×1	10^{-2}	300	10
	—	7×10^{-1}	590	20
	1×1		590	Seconds

In the case of Ge, the oxygen covered surface (10^{-1} torr mm) was heated to 360°C and 450°C for several minutes without the pattern being restored. Heat treatment at 550°C for several minutes did restore the integral orders. The 1×1 structure remained after heating at 690°C and 800°C for a few seconds. The crystal was then heated at 200°C in an atmosphere of oxygen (10^{-5} torr) and then heated at 300°C in the presence of oxygen at pressures of 10^{-4} torr and 10^{-2} torr. The 1×1 structure was unaffected by these treatments. However, this 1×1 structure disappeared when the crystal was heated at 590°C in an atmosphere of oxygen (7×10^{-1} torr). Further heating at 590°C (without further exposure to oxygen) caused the integral order spots to be restored. These results are summarized in table 1.

c) *Intensity measurements* ·

Twelve separate measurements of the variation of intensity with voltage were taken of the (00) spot on different silicon samples, as the specular reflection

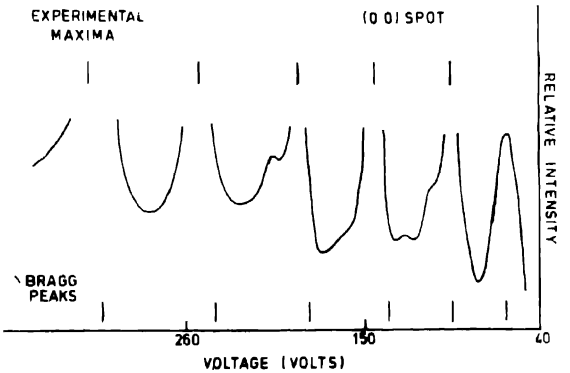

Fig. 3. Intensity Vs Voltage curve of the (00) spot.

measurements are often useful for theoretical analysis and these are shown in figure 3 Ten separate measurements (figure 4) were also taken of the strong (20) integral order spot as this spot was used for oxygen exposure experiments ·

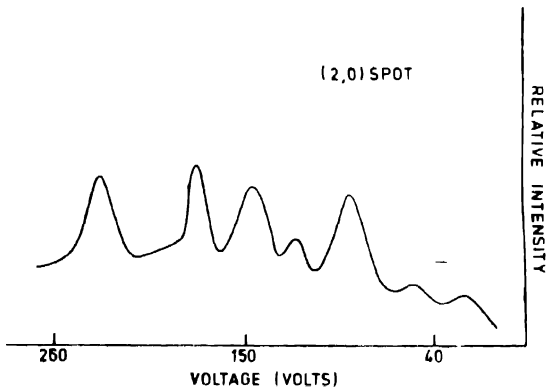

Fig. 4. Intensity Vs Voltage curve of the (20) spot.

Oxygen was exposed to several cleaved Si surfaces and intensity measurements of the (20) spot were made after each exposure. Figure 5 shows plots of the major intensity peaks of the (20) spot spectrum with increasing oxygen exposure. In figures 6 and 7 the intensity curves for two integral order spots (01) and (2$\bar{1}$), and also two 1/2 order spots ($\bar{3}$0) and (11) are presented.

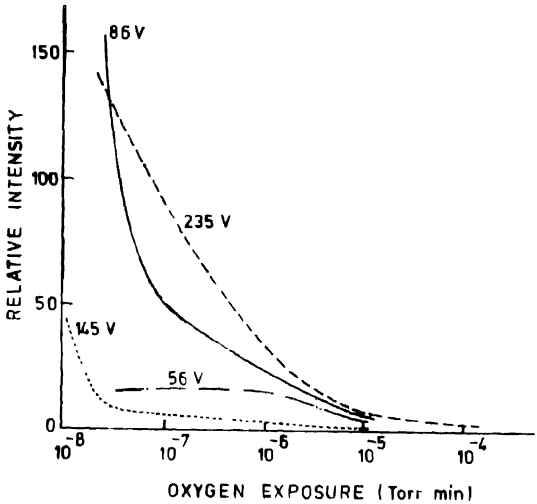

Fig. 5. Plots of the major intensity maxima of the (20) spot intensity curve with oxygen exposure

4 Discussion

The surfaces of both silicon and germanium were found to be very sensitive to small exposures of oxygen. Initially the 1/2 orders were as intense as the integral orders (figures 6 and 7) but they completely disappeared by 5×10^{-7} torr min exposure of oxygen. Exposing the cleaved silicon surface to iron and nickel (Ridgway & Haneman 1971a, 1971b) gave similar results with the fractional orders rapidly weakening.

The gradual extinction of the integral order spots with oxygene xposure would suggest that an amorphous layer was forming on the surface thick enough to cause complete extinction of the LEED pattern at 10^{-1} torr min exposure. That the 1/2 orders weakened and disappeared more quickly than the integral orders may suggest that the oxygen atoms initially assume the ordered bulk lattice positions of the substrate or may cause the silicon surface atoms to relax

back to their normal bulk positions. It is also possible that the molecules may prefer bridge sites as has been proposed by Ibach & Rowe (1974a, 1974b). For different orientations and types of bridge sites, this could also give a disordered structure. This may possibly explain the different rates of change of the peaks of the (2, 0) spot spectrum with oxygen exposure (figure 5).

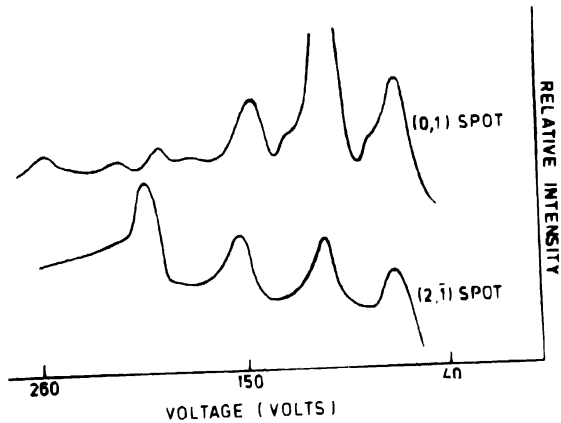

Fig. 6. Intensity Vs Voltage curves of the (01) and (2$\bar{1}$) spots.

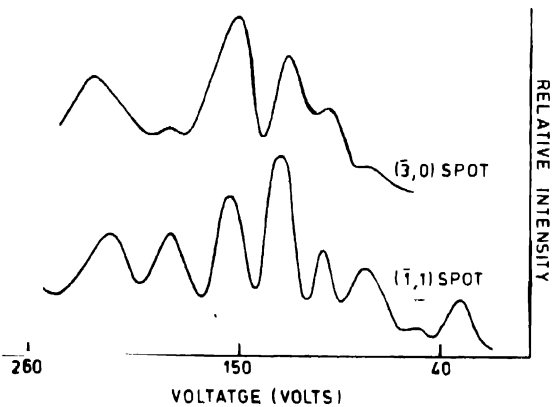

Fig. 7. Intensity Vs Voltage curves of the ($\bar{3}$0) and ($\bar{1}$1) spots.

The present data supports a model of the cleaved surface of Si and Ge proposed by Haneman (1968) in which he considered two kinds of atom sites on the surface. From EPR measurements on aligned cleavage faces of Si, which are cleaved and examined under ultra high vacuum, Haneman suggested one atom site did not contribute to the resonance but was active towards adsorption and the other atom site contributed to the small resonance but was relatively inactive towards adsorption.

He further found the observed resonance signal increased in height (45%) after exposure to 10^{-1} torr min of oxygen. This was the same exposure at which the LEED pattern disappeared in the present experments. It would appear that at low oxygen exposures the oxygen adsorbs onto lowered atom sites which do not contribute to the spin resonance signal resulting in the 1×1 structure. At the high oxygen exposures it would appear that the oxygen is also adsorbed on to the raised atom sites causing both the observed increase in the resonance signal and the extinction of the LEED pattern.

The first model proposed for the cleaved surface of Si and Ge was that of Lander, Gobeli & Morrison (1963, 1965). This model was based on "high-frequency" components in the intensity data and the observed one fold symmetrical nature of the LEED pattern in the y direction. Their intensity measurements were mainly visual (there being only one spot photometer curve shown for the $(\bar{1}1)$, $(1\bar{1})$ and $(\overline{11})$ spots. The present data would indicate this asymmetry is not present. Both the photometric measurement (figure 6) and the LEED photos at numerous voltage settings obtained from the cleaved surfaces, indicated a definite symmetry about the X-direction (figure 2). As a consequence the model proposed by Lander, Gobeli and Morrison does not appear to be compatible with the present data or the EPR measurements (Haneman 1968).

The model proposed by Haneman (1964, 1968) (illustrated in figure 8 without the oxygen atoms) has raised and lowered surface atoms being arranged in rows. It will be noticed that this model is symmetrical about the (10) direction and would therefore fit the present LEED results and intensity data. Recently (Chiarotti & Nannarone 1976) it has been reported that electric field modulation of internal reflection on cleaved Ge (111) 2×1 surfaces results are consistent with this model. It has also been suggested that soft surface phonons and also exciton-phonon interactions can cause lattice distortions resulting in superlattices (Tosatti 1975). Dynamical considerations would then have to be taken into account when considering the intensity data to determine the validity of these models.

With respect to the intensity data, the primary Bragg peaks can be determined from theoretical plots of the surface grating condition ($n\lambda = d \sin\theta$) and the depth grating condition. These peaks are indicated in figure 3. The inner

potential of the silicon (111) surface could be determined from the displacement V' of the measured and calculated peaks in the intensity data obtained from the cleaved surfaces. The inner potential is given by

$$V_i = V + V_c$$

where V_c is the contact potential difference between the cathode of the gun and the crystal. Taylor (1966) measured the value of V_c for his system (tungsten crystal and Varian gun cathode) and found it to be 3·7 V. Since the work function of the cleaved surface of Si (4·8 eV as obtained by Allen & Gobeli 1964) is almost the same as that of W (4·5 eV) and Varian LEED optics were used in these experiments, it was assumed $V_c \sim 4$ V. For the voltage range (20–300 V, figure 3), V' was about 10 Volts. This gives an approximate average value for the inner potential of the Si (111) surface of about 14 V.

The intensity measurements for both the (00) and (20) spots (figures 3 and 4) revealed extra peaks that appeared not to be associated with primary Bragg peaks. Some of these extra peaks were sensitive to the background pressure and were quite possibly associated with the uppermost surface layer. Multiple scattering can account for new spots and modified intensity of the primary beams when the surface layer has a different lattice constant to the underlying layer. If in the present experiments, the cleavage process caused the uppermost layer of atoms to be shifted slightly out of register with the substrate with a resulting change in the lattice constant, multiple scattering may account for some of the observed phenomenon.

The $\sqrt{3} \times \sqrt{3}$ (R30°) structure observed on silicon after the surface had been exposed to 10^{-1} torr min. of oxygen followed by heat treatment at 920°C for 35 minutes has not previously been reported. One possible model for this structure is shown in figure 8 where the adsorbed oxygen atoms are covalently bonded directly over the substrate atoms. Then on further exposure (10^{-6} torr min) oxygen is adsorbed on to the present oxygen sites, relieving the bonded oxygen atoms and allowing the structure to relax back to the (1×1) state.

Haidinger & Barnes (1970) had identified the Si (111) 7×7 structure as containing oxygen in the surface. However oxygen on the 7×7 structure will extinguish the pattern. To solve this dilemma they had introduced an additional Si–O lattice-bonded phase that was ordered. However recent experiments have demonstrated (Ridgway & Haneman 1969, Ibach & Rowe 1974b) that no impurities are identified with the 7×7 structure. Further the fact that a $\sqrt{3} \times \sqrt{3}$ (R30°) structure has been observed when the surface has been explicitly exposed to oxygen makes it much more suggestive that this structure is due to oxygen rather than the 7×7 structure.

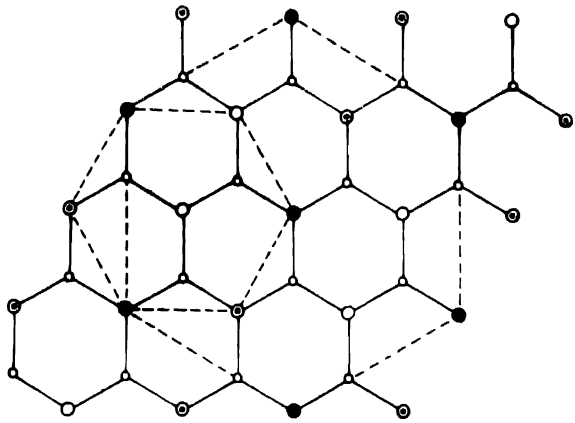

Fig. 8. One possible surface model for the $\sqrt{3} \times \sqrt{3}$ (R30°) structure observed on the oxygen covered heated surface of silicon

Acknowledgements

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